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INTERNAL REPORT MS-65-70

STANDARD METHODS OF SAMPLING, TESTING AND ANALYSIS OF METAL-BEARING ORES AND RELATED MATERIALS

"Highlights of the Work of A.S.T.M. Committee E-16"

by

R.C. McAdam

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ABSTRACT

A.S.T.M. Committee E-16 "On Sampling, Testing and Analysis of Metal Bearing Ores and Related Materials" was formed to promote knowledge of, and to formulate methods for, the sampling, analysis and testing of natural and processed metal-bearing ores and related raw materials such as fluxes. Analytical methods for the determination of iron and silica in iron ores and manganese in manganese ores which were tested and evaluated by the committee have been published as tentative standards in the A.S.T.M. Book of Standards, Part 32, "Chemical Analysis of Metals", 1965. Analytical methods under consideration as tentative standards include: the determination of iron and silica in manganese ores; chrome, iron and silica in chrome ores; silica in fluorspars; phosphorus and an alternate iron method in iron ores.

Physical testing methods for the screen analysis of metal-bearing ores and related materials and tumbler testing of iron-ore agglomerates have also been prepared. A tentative method for sampling and preparation of iron ores, submitted by the sampling sub-committee, has been returned to the Iron Ore Task Force for reconsideration in conjunction with data

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collected by the International Organization for Standardization on bulk sampling of iron ores and preparation of samples for the laboratory.

INTRODUCTION

On June 2, 1959, a conference on sampling and analysis of metallic ores was held in Philadelphia with a representative from the A.S.T.M. Administrative Committee as Chairman. As a result of this conference a steering committee was set up and met on October 1, 1959, to outline the scope and organization of a new committee to be designated E-16.

Fifty-five representatives from government and industry met at an organizational meeting held at A.S.T.M. Headquarters on January 13, 1960. The Steering Committee suggested the title for the new committee to be "Committee E-16 on Sampling and Analysis of Metal Bearing Ores and Related Materials" with the following scope:

"The promotion of knowledge of and the formulation of methods for sampling, analysis, and testing of natural and processed metal-bearing ores and related materials such as fluxes, etc. This work is to be coordinated with the work of relevant committees in A.S.T.M. and other organizations."

The committee title and scope as suggested by the Steering Committee was adopted, a slate of four officers elected, and a temporary executive sub-committee appointed. Regular meetings of Committee E-16 have been held during the annual meetings of the A.S.T.M. and additional meetings during Committee Week of the society.

The committee is composed of five sub-committees, an Executive Sub-committee, and four operational sub-committees, i.e. Sub-Committee I, Editorial and Definitions; Sub-Committee II, Sampling; Sub-Committee III, Analysis and Sub-Committee IV, Testing (Physical).

Late in 1961, Committee E-16 was asked by the American Standards Association to consider the formation of a group to participate in the activities of the International Organization for Standardization, Technical Committee 102, Iron Ores. The proposal was considered in detail by the Executive Sub-committee at the Dallas and New York meetings. As a result a new sub-committee named: U.S.A. National Committee for ISO/TC-102 was set up at the spring committee meeting at Montreal in 1963. The membership of the new sub-committee consists of task force and sub-committee chairmen engaged in iron-ore work plus such other members deemed necessary to fulfil the duties of the sub-committee.

SAMPLING AND PHYSICAL TESTING

Sub-committee I, Editorial and Definitions

The Editorial and Definitions Sub-committee prepared the by-laws for the operation of Committee E-16, which were adopted in 1961, and revised in February 1964 to comply with revisions of the Society, i.e., "Regulations Governing A.S.T.M. Technical Committees".

Tentative methods submitted to the A.S.T.M. for publication have been edited by this sub-committee as well as methods submitted to ballot at committee level.

Sub-committee II, Sampling

This sub-committee is made up of five task forces, Iron Ore, Manganese Ore, Chrome Ore, Fluorspar, and Statistics. Investigations of sampling methods used by various task force members and of standard methods adopted or proposed by national and international standards organizations are underway.

Sampling of Iron Ore

A tentative method for sampling and preparation of iron ores was drafted and voted on at committee level. At least one negative ballot was received as well as numerous comments and the method was withdrawn for further consideration. This procedure described mechanical and manual techniques for sampling natural and beneficiated iron ores. The Iron Ore Task Force with the collaboration of the manganese, chrome and fluorspar task forces plan to replace this method with two sampling procedures for iron ore. The first method will describe sampling from a moving or stationary conveyor belt and the second method will cover other sampling techniques. ISO data which is now available on sampling and preparation of iron ores will be considered in drafting the new methods.

Sampling of Manganese Ore

Prior to the decision of this task force to assist the Iron Ore Task Force in drafting sampling methods, sampling procedures being used by the members as well as standard sampling methods adopted by ISO/TC-65 were investigated. A very complete study was made of belt sampling techniques on a cargo of manganese ore and further data were obtained on

belt sampling from other members of the task force. The data obtained plus information on grab bucket and manual sampling were given to the statistical task force of the sampling sub-committee for interpretation. This study led to some valuable conclusions concerning a two-stage sampling plan and its effect on sample size, size and frequency of increments, and variation between increments.

Sampling of Chrome Ore

The Chrome Ore Task Force studied sampling methods on three cargoes of chrome ore. These studies were arranged so that comparisons could be made between top-of-car sampling at ship-side and top-of-car sampling enroute, belt sampling at dock-side and automatic plant sampling, belt sampling at dock-side and manual sampling from barges. Analytical results on one cargo were given to the Statistical Task Force for evaluation. At present the chrome ore sampling group is co-operating with the Iron Ore Task Force in drafting of sampling methods. The iron ore methods will be subsequently adapted to chrome ore sampling.

Sampling of Fluorspar

This group has drafted a general bulk ore sampling method for study at sub-committee level. The Fluorspar Task Force has also been supplying data and assistance to the Iron Ore Tasi: Force and hopes to adapt the methods developed to its own particular needs.

It should be observed that, due to the existence of ISO groups which are carrying out investigations of sampling procedures for iron and manganese ores, a considerable amount of data is available for study in

setting up standard techniques for sampling these ores. Chrome ores and fluorspar, however, are not under study by ISO groups and because of this, it may be easier, after the establishment of satisfactory methods for sampling iron ore, to adapt them to chrome ore and fluorspar.

Sub-committee IV, (Physical) Testing

This sub-committee was organized with the objective of developing physical testing methods for natural and processed metal-bearing ores and related raw materials. Such methods include sieve analysis, grindability, hardness, friability, strength, reducibility, etc. Methods for sieve testing of ores and related materials, and a tumbler test for iron agglomerates were considered of prime importance. Fourth drafts of both methods were approved at task force level and were submitted to the Editorial and Definitions Sub-committee. The methods were edited and submitted to letter ballot at committee level. One or two negative votes were recorded; when the problems respecting these are resolved the methods will be submitted to the A.S.T.M. as tentative standards.

Tentative Methods of Test for Particle Size or Screen Analysis at No. 4 Sieve and Finer for Metal-Bearing Ores and Related Materials

The methods describe procedures for determining size distribution by screen analysis, dry or wet, at No. 4 sieve and finer. The dry screening technique may be used on any solid particles which can be dried so that sieve blinding does not occur; the wet screening technique, using liquid media may be used on any insoluble solids. Sieve blinding may occur when particles of the material become jammed in the sieve openings.

Particles which are soft in texture or have irregular shapes may cause this difficulty. The sieves referred to are U.S. Standard sieves according to the standard specifications for sieves for testing purposes, designation E-11-61 of the American Society for Testing and Materials.

Following a glossary covering some of the terms referred to, the methods are described under the following sub-divisions:

1. Apparatus.
2. Preparation of the sample for screen analysis.
3. Sample size (sieve loading).
4. Drying of the sample for dry screening.
5. Time of screening.
6. Evaluating results and reporting.
7. Degradation during screening.
8. Wet screening.
9. Calibration of sieves.

As these methods will be published as tentatives very shortly, it is not the author's intention to go into a detailed discussion of them. The conclusions of the task force which prepared the methods are, however, worthy of note:

a) It is generally agreed that errors in screening arise from the way in which screening is done. Selection of the sample loading of the sieves, sieves themselves, and the final weighing, all influence the reproducibility or accuracy of screening.

b) The theory of probability with respect to a particle passing a

sieve opening is a factor of a statistical nature which exercises great influence on screening results. The size and shape of the particles are factors to be concerned with in the low probability of the particle passing the screen when particles are nearly equal in size to screen apertures.

c) Screening time is important but it cannot be said that a specific time of screening should be used for all types of materials. End point or time of screening for different materials is to be established by experimentation to meet the requirements of the specific material.

d) Recognition of the potential errors that exist in screening should result in more accurate annalysis.

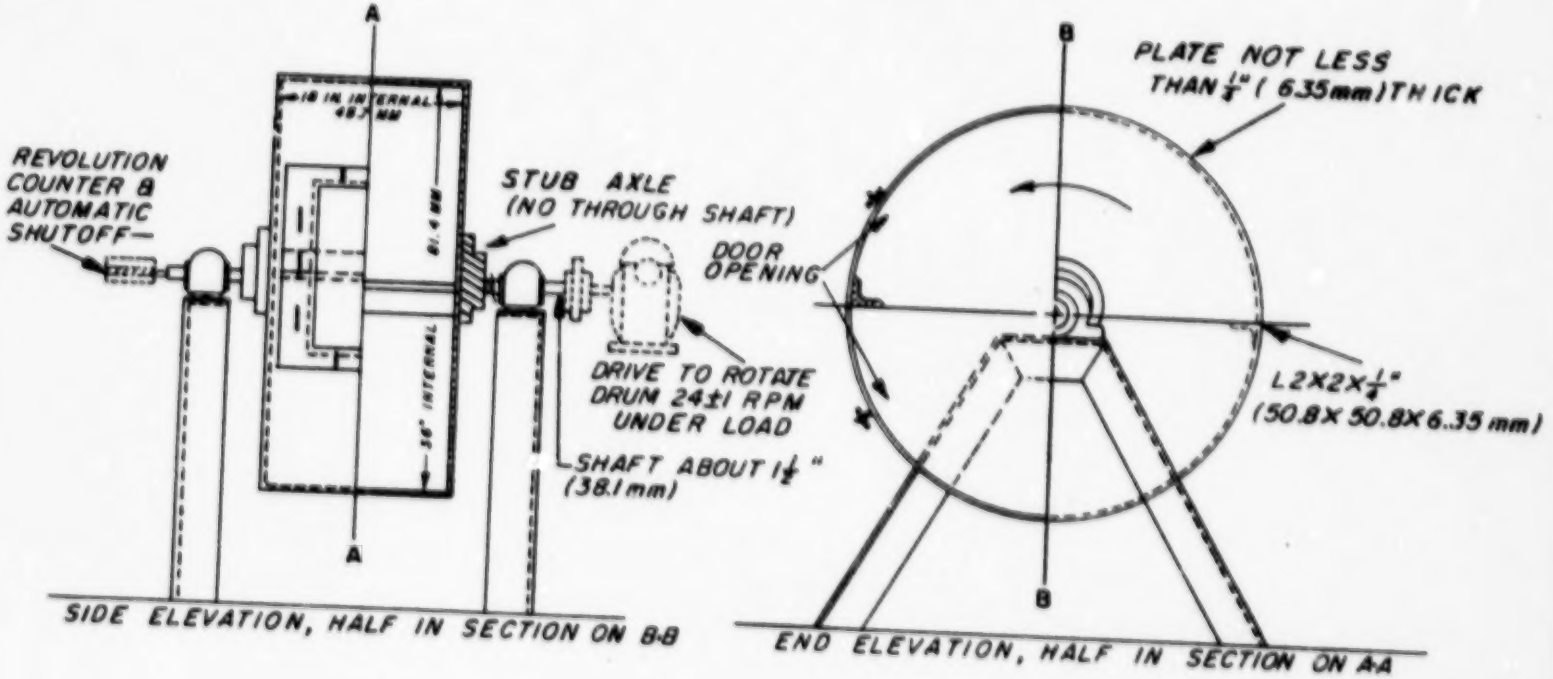
Tentative Method of Tumbler Test for Iron Ore Pellets and Sinter

This method provides a relative measure of the resistance of iron-ore pellets and sinter to degradation by impact and by abrasion.

The tumbler machine used for this test is shown in Figure 1.

Two equally spaced 2 x 2 x $\frac{1}{4}$" angles attached longitudinally inside the drum lift the sample as the drum is rotated through 200 revolutions at 24 $\pm$1 rpm. The sample is then removed from the drum and hand sieved on $\frac{1}{4}$-inch (6.35 mm) and No. 30 sieves (595μ). Mechanical sieving may be used provided it has been established that the method gives the same results as hand sieving.

Two tests shall be made on pellet and sinter samples. For pellets, if differences between the values obtained exceed 0.4 units in the cumulative percentage of pellets over the $\frac{1}{4}$ inch (6.35 mm) or the No. 30 sieve (595μ), a third test shall be made and the mean value of all tests taken.


A
A
B
B
REVOLUTION COUNTER & AUTOMATIC SHUTOFF—
STUB AXLE (NO THROUGH SHAFT)
DOOR OPENING
DRIVE TO ROTATE DRUM 24±1 RPM UNDER LOAD
SHAFT ABOUT 1½" (38.1 mm)
PLATE NOT LESS THAN ¼" (6.35mm) THICK
L 2X2X¼" (50.8X50.8X6.35 mm)
SIDE ELEVATION, HALF IN SECTION ON B-B
END ELEVATION, HALF IN SECTION ON A-A

TUMBLER TEST APPARATUS

Figure 1.—Tumbler Ma

For sinters, if the differences between the values exceed 2.0 units in the cumulative percentage of material over the $\frac{1}{4}$ inch (6.35 mm) or the No. 30 sieve (595μ), a further test shall be made and the mean value of all tests taken.

The total loss in weight in any one test may not exceed 0.7 weight per cent of the initial sample weight (0.175 pound (79.1 g) for a 25.0 pound (11.3 Kg) sample.

The sieve analysis after tumbler test shall be reported to the nearest 0.1 per cent as follows: per cent on $\frac{1}{4}$ inch and per cent passing No. 30 sieve.

SUB-COMMITTEE III ANALYSIS

Iron Ore

Standards Issued

Tentative methods submitted by A.S.T.M. Committee E-16 that have been published in the A.S.T.M. Book of Standards, Part 32, "Chemical Analysis of Metals, Sampling and Analysis of Metal-Bearing Ores, 1965", include the following: "The Determination of Total Iron in Iron Ores by Hydrogen Sulfide Reduction and Dichromate Titration", and "Silica in Iron Ores".

The basis of the method for the determination of total iron was the findings of the "Methods of Analysis Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association". In paper MG/D/23/52, "The Determination of Iron in Ores, Slags and Refractories", the results of a study on the hydrogen sulphide reduction

method versus the stannous chloride reduction procedure are reported. The conclusion given in the paper is that the hydrogen sulphide reduction method, which is not subject to interference from other metals such as platinum, molybdenum, copper, and vanadium, has a more general application than the stannous chloride reduction procedure. The hydrogen sulphide method is affected by large amounts of phosphate, nitrate, fluoride or chloride. The latter three acid radicals are easily removed by evaporating to fumes of sulphuric or perchloric acid before the reduction; however, phosphoric acid must not be used in the initial treatment and may only be added after the reduction of the ferric iron. The Iron Ore Task Force (E-16) evaluated the method on four different types of iron ore plus an N.B.S. standard ore. Table 1 gives the results obtained by nine laboratories which supplied data.

Iron values submitted by the Mineral Sciences laboratories are given under laboratory "C" in Table 1 and are in reasonable agreement with the laboratory averages for the test ores. Russelville ore, which shows the greatest range of values, may tend to pick up moisture when exposed to air during the weighing of the sample. The weighing technique for iron ores will be changed in all tentative methods before they are adopted as standard methods.

In the determination of silica in iron ores the sample is treated with hydrochloric acid and fumed with perchloric acid. The insoluble residue is separated by filtration, ignited, fused with sodium carbonate and the melt dissolved in the filtrate. The silica is separated by a double

TABLE 1 - Laboratory Results for Iron Determination

Laboratory	Chilean Iron Ore	Seine River Ore	Knob Lake Ore	Russelville Iron Ore	N.B.S. Iron Ore
A	66.27	57.43	58.65	51.29	27b - 68.25
B	66.07	57.43	58.45	50.94	27d - 64.94
C	65.98	57.48	58.39	50.84	27d - 64.93
D	66.14	57.55	58.42	50.92	27d - 65.11
E	66.15	57.63	58.36	50.74	27d - 65.05
G	65.91	57.48	58.34	50.86	27c - 64.95
H	66.19	57.59	58.40	51.01	27d - 65.03
J	66.32	57.63	58.61	50.74	27d - 64.96
K	65.86	57.49	58.39	50.92	27c - 64.99
Laboratory Average	66.10	57.52	58.45	50.92	
Range of Values	65.86 to 66.32	57.43 to 57.63	58.34 to 58.65	50.74 to 51.29	

N.B.S. Certificate Values

27b - 68.25

27c - 65.00

27d - 64.96

dehydration with perchloric acid, the precipitates combined, ignited, and weighed. The silica is volatilized by treatment with sulphuric and hydrofluoric acids, and the residue ignited and weighed.

At a recent meeting of ISO/TC-102, Iron Ores, at least one European delegate reported the presence of fluorine in his iron ore.

Silica, if present in the form of silicates, will be volatilized by the fluorine present if this method is used. Silica in the form of quartz will not be affected by the fluorine. An ore of this type will require a method in which the fluorine has been complexed in order to obtain true silica values. Table 2 gives the data obtained by nine laboratories in carrying out silica determinations by the tentative method. Mineral Sciences laboratories values are given under Laboratory C.

TABLE 2 - Laboratory Results for Silica Determination

Laboratory	Chilean Iron Ore	Seine River Ore	Knob Lake Ore	Russelville Iron Ore	N.B.S. Iron Ore
A	3.66	8.91	8.44	10.67	27d - 2.21
B	3.56	8.84	8.39	10.66	
C	3.61	8.76	8.31	10.49	27d - 2.05
D	3.58	8.68	8.39	10.46	27d - 2.04
E	3.60	8.85	8.41	10.57	27d - 2.10
G	3.48	8.70	8.19	10.35	27c - 2.08
H	3.54	8.88	8.38	10.53	27d - 2.07
J	3.60	8.76	8.45	10.47	27d - 2.17
K	3.65	8.82		10.68	27c - 2.08
		- - - - - - - - - - - -			
Laboratory Average	3.59	8.80	8.37	10.54	
Range of Values	3.48 to 3.66	8.68 to 8.91	8.19 to 8.45	10.35 to 10.68	

N.B.S. Certificate Values

27c - 2.08

27d - 2.10

Table 2 shows that there is good agreement in the silica results obtained by the nine contributing laboratories. The Russelville ore, once again, gave the greatest range of values.

Work in Hand

Iron in Iron Ores

As an alternative to the H_2S procedure, a method for the determination of total iron in iron ores by stannous chloride reduction and dichromate titration has been approved by committee E-16 and will be submitted as a proposed tentative method to the A.S.T.M. The method is applicable to iron ore samples containing less than 0.10 per cent copper, vanadium or molybdenum. The sample is dissolved in hydrochloric acid and any insoluble residue is separated by filtration, ignited and treated for the recovery of contained iron which is then added to the main solution. Ferric iron is reduced with stannous chloride in slight excess. The excess is oxidized in the cold by the addition of mercuric chloride solution, H_2SO_4-H_3PO_4 mixture is added, and the ferrous iron is titrated with standard potassium dichromate solution using sodium diphenylamine sulfonate as an internal indicator. This procedure gives a rapid and accurate method when the interferences, previously mentioned, do not exceed the prescribed limit.

Phosphorus(Alkalimetric) in Iron Ore

A procedure for the determination of phosphorus in iron ores, concentrates and agglomerates in the concentration range 0.01 to 1.00 per cent has been tested by the Task Force. In the method the sample is dissolved in hydrochloric and nitric acids and, after the addition of perchloric acid, taken to strong fumes to dehydrate the silica. The insoluble residue is treated for the recovery of any contained phosphorus which is then added to the main solution. After adjustment of volume and temperature, ammonium molybdate is added to precipitate yellow phospho-molybdate. The sample is shaken thoroughly and allowed to stand to ensure complete precipitation. The precipitate is filtered off and after washing free of acid, is dissolved in an excess of sodium hydroxide solution. The excess sodium hydroxide is titrated with a standard solution of nitric acid using phenolphthalein as an indicator. Hydrochloric, sulphuric and hydrofluoric acids or salts of these acids retard the formation of the yellow precipitate and should be avoided. Vanadium and arsenic coprecipitate with the phosphorus and provisions for their removal are included in the procedure. The arsenic is volatilized using HBr and taking to fumes of perchloric acid. If vanadium is present it is reduced by the addition of ferrous sulphate solution. Titanium tends to form an insoluble compound with phosphorus and may cause low values. However up to 0.5 per cent TiO_2 causes no significant error and in the method, as written, any titanium which is present in the residue is separated from the phosphorus by filtering from the alkaline solution after

fusing with sodium carbonate. Table 3 gives the data obtained by the laboratories which tested and evaluated the method. As before, "C" designates Mineral Sciences laboratories.

Table 3 - Laboratory Results for Phosphorus Determination

Laboratory	Chilean Iron Ore	Seine River Ore	Knob Lake Ore	Russelville Iron Ore	N.B.S. Iron Ore
A	.043	.030	.085	.601	27d - .028
B	.046	.032	.086	.581	
C	.046	.029	.083	.601	27d - .026
D	.043	.032	.085	.612	27d - .029
E	.041	.028	.083	.595	27d - .028
G	.041	.031	.084	.599	27c - .028
H	.045	.028	.085	.588	27d - .028
J	.046		.082	.606	27d - .028
K	.043	.031	.086	.601	27c - .028
L		.030	.087		27c - .030
N	.043	.030	.085	.595	27d - .028
Laboratory Average	.044	.030	.085	.598	
Range of Values	.041 to .046	.028 to .032	.082 to .087	.581 to .612	

N.B.S. Certificate Values

27c - .028

27d - .028

As shown by the data obtained in Table 3, the proposed method gives satisfactory results for the determination of phosphorus. After the objections raised by the one negative ballot are resolved by the committee this method will be submitted to A.S.T.M. as a tentative standard.

Manganese in Iron Ores

Two methods for the determination of manganese in iron ores are under study by members of the Iron Ore Task Force.

1. The Photometric Periodate Method

This method covers the determination of manganese in the concentration range of 0.01 to 5.00 per cent. Varying combinations of the iron ores previously submitted by A.S.T.M. Committee E-16 were analysed. Results by the proposed method show reasonable precision and when all laboratories have submitted their values the method will be evaluated.

2. The Pyrophosphate (Potentiometric) Method

Manganese in the concentration range from 2.5 to 15.0 per cent may be determined by this method. Two manganiferous iron ores and a Chilean ore, submitted by A.S.T.M. Committee E-16, were used to make varying combinations of samples. Initial results obtained by the Mineral Sciences laboratories by this method on the manganiferous iron ores indicated a high sensitivity of the samples to atmospheric humidity. A sample of manganiferous ore (5.2% Mn) was submitted to the Physical Chemistry Section of the Mineral Sciences Division for X-ray diffraction, differential thermal and thermogravimetric analyses. The ore proved to be

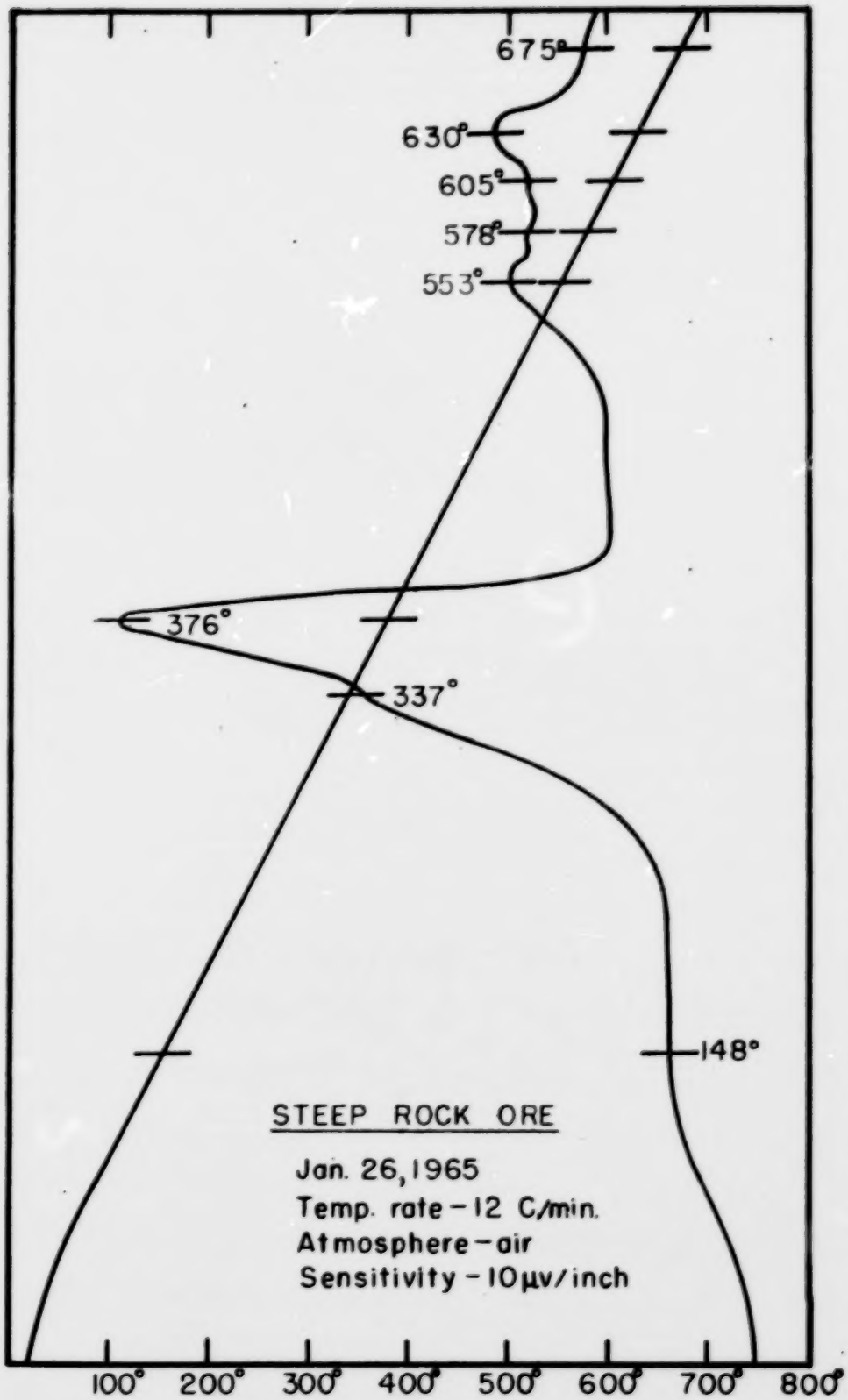


Figure 2 - Differential thermal curve

very hygroscopic and Figure 2 and Table 4 give the results obtained by differential thermal and thermogravimetric analysis of this sample.

When a constant temperature increase of 12°C/min. was reached on the differential thermal curve at 75°C an endothermic reaction was recorded which indicated a weight loss due to moisture being driven off. The endothermic reaction recorded in the 376°C range is caused by the water loss from the hydrated iron oxide which makes up the bulk of the sample. Other points on the curve were not identified but may be due to the presence of silica, manganese carbonate, etc.

Table 4 - Thermogravimetric Analysis of Manganiferous Iron Ore (5.2% Mn)

Initial weight of sample	799.5 mg
Weight after heating to 220°C	792.1 mg
Loss	7.4 mg = 0.93%
Sample reweighed after standing overnight in air	796.5 mg
Previous sample weight	792.1 mg
Gain	4.4 mg

Weight regained = $\frac{4.4}{7.4} \times 100 = 60\%$ (approx.) of original loss

Weight of sample	796.5 mg
Weight after reheating to 220°C	792.5 mg
Loss	4.0 mg
Weight of sample after standing in air for 2½ hours	795.9 mg
Previous sample weight	792.5 mg
Weight regained	3.4 mg

Table 4, which gives the results obtained in a thermogravimetric analysis of the sample, indicates the effect which atmospheric humidity has on chemical analysis if a proper weighing technique is not used.. In an acceptable procedure the sample must be dried at 105 - 110°C in a weighing bottle, capped and cooled in a desiccator and then the bottle and contents weighed. The sample is then transferred to a beaker, the bottle restoppered and reweighed. The difference in the weight is the weight of the sample taken. Due mainly to the results of these differential thermal and thermogravimetric analyses, all tentative methods for iron-ore analyses will be modified to incorporate this weighing procedure.

Phosphorus (Photometric) in Iron Ores

The determination of phosphorus in iron ores by a photometric vanadomolybdic acid method is being evaluated by the Iron Ore Task Force. This method provides for the determination of phosphorus in iron ores, concentrates and agglomerates in the concentration range 0.002 to 1.00 per cent. The sample is dissolved in HCl, HNO_3 and $HClO_4$, and evaporated to fumes. The residue is taken up in water and any insoluble material separated by filtration and treated for recovery of any contained phosphorus. The yellow coloured complex of phospho-vanado-molybdic acid is formed by the addition of ammonium vanadate-ammonium molybdate solution, extracted into iso-butyl alcohol and the absorbance measured at 425 mμ. Preliminary results obtained in the Mineral Sciences laboratories by this procedure indicate that aliquots of

a standard phosphorus solution should be run simultaneously with the samples using the same solutions and colour development time to give a satisfactory calibration curve. Iron interferes in this method when absorbance is measured at 425 mμ and more care may be required in the adjustment of the acidity of the sample for proper extraction with iso-butyl alcohol. Table 5 gives the results obtained on five iron ores by the colorimetric and gravimetric methods.

Table 5 - Phosphorus by Photometric and Gravimetric Methods

Sample	Photometric Vanado-Molybdic Acid Method (Mineral Sciences Laboratories		Alkalimetric Method
Seine River Ore	0.033	0.031	0.030*
Russelville Ore	0.602	0.592	0.598*
Chilean Ore	0.042	0.044	0.044*
Knob Lake Ore	0.085	0.084	0.085*
N.B.S. 27d	0.027	0.029	0.028*

*Task Force laboratory averages.

The agreement shown between values obtained by the two methods indicates that the photometric technique for the determination of small amounts of phosphorus in iron ores may be very useful.

Projected Work

The Iron Ore Task Force of Sub-committee III (Analysis) has carried out testing and evaluating of methods since its organization in June 1961. Two methods are already published with several others nearing this stage. Methods still to be investigated include the

determination of sulphur and aluminum. The determination of sulphur by combustion and gravimetric methods has been discussed and an investigation of these procedures will start in the near future. The volumetric and gravimetric method, using hydroxy-quinoline, for the determination of aluminum which is being investigated by ISO/TC 102, Iron Ores, will be submitted to task force members for evaluation.

Manganese Ores

Standards Issued

A tentative method for the determination of manganese in manganese ore by the pyrophosphate (potentiometric) method has been published in the A.S.T.M. Book of Standards, Part 32, 1965. It is based on a method by Lingane, J.S. and Karplus, R, Anal. Chem. 18, 191 (1946). In this procedure the manganous ion is titrated potentiometrically with permanganate ion in neutral pyro phosphate solution. The method is applicable without any separations to a wide variety of manganiferous metallurgical products and yields accurate results.

Manganese ores are decomposed by hydrochloric, nitric, hydrofluoric and perchloric acids (insoluble residue, if present, may be fused with sodium carbonate) and after the addition of sodium pyrophosphate and adjustment of the acidity the manganese is determined by oxidation of manganous (+2) to manganese (+3) with a standard solution of potassium permanganate. Chromium, which may interfere, is volatilized from the perchloric acid solution by the addition of small amounts of hydrochloric acid.

Work in Hand

Methods for the determination of iron and silica in manganese ores have been tested and evaluated by the task force and are ready for balloting at sub-committee level. A photometric method for the determination of phosphorus in manganese ores is being investigated and data compiled.

Silica in Manganese Ores

This method is very similar to the method published for silica in iron ores. The silica is separated by double dehydration with perchloric acid and then volatilized with hydrofluoric acid. None of the elements normally found in manganese ores interfere in this procedure.

Iron in Manganese Ores

The tentative method for the determination of iron in manganese ores in the range of 2 to 20 per cent is based on the published tentative method for the determination of iron in iron ores. Interfering elements such as copper, molybdenum, etc., are separated as the sulphides.

Phosphorus in Manganese Ores

The sample is dissolved in HF and HNO_3 and fumed with $HClO_4$. Phosphorus is recovered from any siliceous residue by fusion with Na_2CO_3. The resulting solution is treated with Na_2SO_3 and ammonium molybdate-hydrazine sulphate solution to develop a coloured complex. Photometric measurement is made at 830 mμ. The phosphorus results by this method have been very erratic and more work is necessary on this procedure.

Projected Work

A discussion of further analytical methods to be evaluated by the task force will be held at the next meeting of Committee E-16.

Fluorspar:

Standards Issued

No tentative standards have been published up to the present.

Work in Hand

The determination of silica in fluorspar was given top priority by the Fluorspar Task Force. Two methods have been tested and evaluated, one a titration procedure and the other a photometric technique.

Silica in Fluorspar (Titration)

This method has been tested for silica concentrations between 0.7 and 8 per cent. The sample is fused in potassium carbonate. The insoluble potassium fluosilicate,which is obtained by treatment of the melt,is purified, decomposed with water, and the resulting hydrofluoric acid is titrated with standard hydroxide solution. None of the elements normally found in fluorspar interfere in this method.

In the determination of silica by this procedure a synthetic standard, containing approximately the same concentration of silica and calcium fluoride as the sample portion to be analysed, is carried through the entire procedure. The titration of this synthetic to obtain the factor for the NaOH solution will give higher silica values than if the theoretical factor is used (NaOH standardized with potassium acid phthalate). This may be due to some solubility or loss of potassium fluosilicate during the

prolonged washing procedure. Results among the contributing laboratories using this procedure are in good agreement.

Silica in Fluorspar (Photometric)

A photometric method which is also under investigation by the task force appears to offer the best approach to solving the problem of determining silica in fluorspar. This method is also used for the determination of silica in fluorspar in the range from 0.7 to 8 per cent. The sample is fused with anhydrous borax and the melt is leached in dilute hydrochloric acid. The silica is determined photometrically from aliquots of this solution. Maximum colour development occurs at pH 0.3 and measurement of the yellow silicomolybdate complex is made at 400 mμ. Due to the fact that no peak occurs on the absorbance vs. wavelength curve obtained for the complex formed, it is advisable to run standard samples simultaneously with the unknowns using the same reagents, etc.

Table 6 gives laboratory results for the determination of silica by the colorimetric and titration methods.

In Table 6 the range of values is greater than might be hoped for using standard methods. However it is noted that the laboratory averages for the two methods are in quite good agreement. With improvement in technique and care in the use of these methods the inter-laboratory agreement may be better. Investigation of both methods is being continued.

Projected work

The task force plans to investigate methods for the determination

TABLE 6 - Silica in Fluorspar by Colorimetric and Titration Methods

Laboratory	Colorimetric		Laboratory	Titration	
	Sample 79(a)	Mexican No. 2		Sample 79(a)	Mexican No. 2
* 1	0.74	6.93	* A	0.70	7.11
2	0.66	6.99	B	0.70	7.13
3	0.73	7.13	C	0.75	7.09
4	0.67	6.97	D	0.71	7.09
5	0.73	7.14	E	0.64	7.08
6	0.68		F	0.63	6.80
7	0.69	7.05	G	0.62	6.93
	Av. 0.70	Av. 7.03		Av. 0.68	Av. 7.03
Range of Values	0.66-0.74	6.93-714		0.62-0.75	6.80-7.13

* Mineral Sciences laboratories

of CaF_2, CaO, MgO, $CaCO_3$ and Al_2O_3 in fluorspar. Procedures for the determination of CaF_2 by the distillation of the fluorine and also by analysing for calcium content will be next in order of priority.

Chrome Ores

Standards Issued

No tentative standards have been submitted by the Chrome Ore Task Force up to the present.

Work in Hand

This task force has evaluated methods for the determination of chromium, iron, and silica in chrome ores. The results which have been received are acceptable, but data has been requested from two or three more laboratories in order to complete the investigations.

Chrome in Chrome Ore

The Cr_2O_3 was determined using the method as published in A.S.T.M. by Refractory Committee C-8. The method is written for the determination of chromium oxide (Cr_2O_3) in chrome ores, concentrates, and finished ore products, such as brick and cement having a concentration variation of 5 to 50 per cent.

The sample is fused with sodium peroxide and the melt leached with water. After the addition of sulphuric acid and oxidation with silver nitrate and ammonium persulphate the chromium VI is reduced by the addition of a measured excess of ferrous ammonium sulphate. The excess of ferrous ammonium sulphate is titrated with standard potassium permanganate or potassium dichromate, using ortho-phenanthroline or

sodium diphenylamine sulphonate, respectively, as an indicator.

Iron and Silica in Chrome Ores

These determinations are of a classical nature requiring fusions to take the sample into solution and subsequent leaching in either water or dilute acid as required. The fusion for iron may be carried out in a zirconium crucible and that for silica in an iron crucible.

Projected Work

The work of the Chrome Ore Task Force has not progressed as rapidly as was hoped, due in part to a smaller number of laboratories contributing results and data. At the last meeting of the committee two or three more laboratories volunteered to assist this group. Methods for the determination of CaO, MgO and Al_2O_3 in chrome ores will be investigated by the Task Force when the methods presently under study are completed.

Advantages of Standards

The results, given in Tables 1 to 6 in this report, show the precision and accuracy which it is possible to obtain using standard methods of analysis. By contrast the following table shows the results obtained for element X by eight laboratories which carried out round-robin analysis on four identical samples using their own methods.

The results in this table show the wide range of values obtained by the participating laboratories. Some of the variations may be due to the use of methods that are subject to interferences which were not eliminated. Weighing errors also appear to be a factor. The effect of random methods is most evident.

TABLE 7 - Round Robin Values for Element X

on Identical Samples

Laboratory	Head Sample	Table Concentrate	Sulphide Concentrate	Table Tails
A	0.50	45.74	2.34	0.55
B	0.51 0.53	22.38 22.59	2.84	0.61 0.63
C	0.59	36.70	2.34	0.67
* D	0.61	46.49	2.41	0.67
E	0.43 0.46	42.20 45.90	2.53 2.28	0.56 0.60
F	0.54 0.56	44.95 44.95	2.29 2.29	0.70 0.69
G	0.93 0.97	47.2 47.1	5.03 5.05	0.82 0.84
H	0.477	46.52	1.98	0.54
Range of Values	0.46-0.97	22.38-47.2	1.98-5.05	0.54-0.84

* Mineral Sciences laboratories

SUMMARY

Since the organization of A. S. T. M. Committee E-16 in 1960, three analytical methods for the determination of iron and silica in iron ores and manganese in manganese ores have been published as tentative standards. Analytical methods for the determination of six other elements and procedures for sieve and tumbler tests have been balloted on within the committee and will be ready for publication very shortly. A total of seven other analytical procedures and four sampling techniques are still being tested and evaluated. As methods are completed and published the

committee plans to extend its work on methods of sampling, testing and analysis to include other properties and constituents of the four ores presently being tested and later to investigate other ores.

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